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ABATEMENT OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES

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A report is presented of a comprehensive study of nitrogen oxides emissions from stationary sources. The report discusses: the sources of nitrogen oxides; formation and control of emissions from combustion sources; stack-gas cleaning, formation and control of emissions from chemical operations, and sampling and analytical methods. It is hoped that this report will be useful in planning and coordinating the research, development, and demonstration programs required to meet the national need for cleaner air.

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ABATEMENT OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES

Prepared by
Ad Hoc Panel on Abatement of Nitrogen Oxides
Emissions from Stationary Sources
Committee on Air Quality Management
Committees on Pollution Abatement and Control
Division of Engineering
National Research Council
National Academy of Engineering

Washington, D.C.
1972

This is the report of a study undertaken by the Committee on Air Quality Management *Ad Hoc* Panel on Abatement of Nitrogen Oxides Emissions from Stationary Sources for the National Academy of Engineering in execution of work under Contract No. CPA 70-48 with the Office of Air Programs of the Environmental Protection Agency.

As a part of the Division of Engineering of the National Research Council, the Committees on Pollution Abatement and Control perform study, evaluation, or advisory functions through groups composed of individuals selected from academic, governmental, and industrial sources for their competence and interest in the subject under consideration. Members of these groups serve as individuals contributing their personal knowledge and judgments and not as representatives of any organization by which they are employed or with which they may be associated.

PREFACE

Americans are justifiably concerned with the deteriorating quality of their physical environment. The determination of government--at the federal, state, and local levels--to reverse this trend is reflected in recently enacted laws and in strengthened enforcement actions. Control of pollution involves technical decisions and economic trade-offs of benefits received for costs incurred, and the decisions that are made will be the wisest if a considerable portion of the concerned public is informed on the problems and the facts that underlie them. This report, which is an assessment of the control technology for a significant air pollutant--nitrogen oxides--is addressed primarily to a technical audience. However, it is hoped that it will have value to others who are concerned primarily with political and social aspects of air pollution control.

In preparing this report the *ad hoc* Panel on Abatement of Nitrogen Oxides Emissions from Stationary Sources met in Washington, D.C. several times over a period of seven or eight months, generally for two-day sessions, during which a large number of experts from government and industry presented information and their views and insights. This was supplemented by review of many technical documents, reports, and papers. All information received was extensively debated by the members of the Panel, each of whom is directly concerned in his professional activities with some aspect of air-pollution control. On this basis, the Panel arrived at a collective judgment, recognizing that knowledge about both the degree of health hazard and the technology of control is increasing rapidly and that current judgments may undergo considerable change within a few years. The goal of the Panel has been to provide a balanced viewpoint, verifiable quantitatively as far as possible, concerning the current status of abatement of nitrogen oxides emissions from stationary sources and what is reasonably achievable in the near future. It is hoped this will be of value to government and to the public in making the complex decisions that lie ahead.

Charles N. Satterfield, *Chairman*

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M. S. Peters, University of Colorado

Staff
R. W. Crozier, *Executive Secretary*, Committees on Pollution Abatement and Control, National Research Council
J. M. Marchello, *Staff Engineer*, Committees on Pollution Abatement and Control, National Research Council
Barbara P. Sowers, *Administrative Secretary*, Committees on Pollution Abatement and Control, National Research Council

Liaison Representative - EPA
Stanley J. Bunas, Division of Control Systems, Office of Air Programs, Environmental Protection Agency

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I

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

A. SUMMARY

National and regional standards for air-quality management are being defined under the Clean Air Amendments of 1970 (Public Law 91-604).[1] Keeping the costs of meeting these standards within bounds and minimizing the burden on our national economy will call for the best efforts and most careful planning at all levels, from individuals, civic groups, and companies to local, regional, state, and federal agencies.

The nitrogen oxides emitted from industrial sources are essentially nitric oxide (NO) and nitrogen dioxide (NO_2). They are generally grouped together and, for convenience, termed NO_x. Nitrous oxide, N_2O, at the levels emitted by most chemical processes, is believed to be innocuous and is not included in the definition of NO_x. About 53 percent of the total man-made NO_x emissions in the United States are from stationary sources. (The remainder is emitted by vehicles.) The largest stationary-source contributions are from the fossil-fuel-fired boilers of electric utilities and from industrial furnaces. At the 1970 level of control, NO_x emissions from stationary sources would approximately double by the year 2000. The need to reverse this trend is clear.

On a world-wide basis, man-made sources of NO_x produce but a tenth of that produced naturally. But the distribution of man-made NO_x is closely related to population distribution; over 60 percent of the emissions in the United States occur in urban areas. The relative contributions from stationary and mobile sources vary substantially from city to city and the proportionate contribution at ground level is presumably more from mobile sources than from stack emissions. Stack height and meteorological factors also affect the relative contributions. NO_x has a residence time in the atmosphere of three to four days. Thus, pollution from NO_x is a regional rather than a global problem.

Unlike emissions of sulfur oxides (SO_x), which are directly proportional to the sulfur content of the fuel, NO_x is formed largely by the reaction of nitrogen and oxygen from the atmosphere at the high temperatures existing during combustion. A smaller contribution is from organo-nitrogen compounds in the fuel. *The most promising prospects for significant early reduction of NO_x in fuel-combustion stack gases lie chiefly in application of some combination of combustion-modification processes to reduce the NO_x formed. The probability that processes can be developed for removal of NO_x from stack gases is not encouraging.*

B. CONCLUSIONS

With regard to combustion-control modification the following conclusions are drawn:

1. Of the three fuels used in firing, gas, oil, and coal, gas allows the most precise control in the attainment of the lowest levels of NO_x. The term "coal" covers a variety of types of solid fuels varying greatly in their combustion characteristics and the nature of the ash formed. A variety of boilers and burners are required to burn these various types satisfactorily. Present emission levels from coal firing vary greatly. Of the three fuels, least is known about coal relative to minimizing NO_x formation from combustion. *A realistic objective for new plants using natural gas to be placed in operation by 1980, is a reduction in NO_x concentration to about 100 ppm from present-day uncontrolled levels, which average about 350 to 400 ppm, but range as high as 1,400 ppm.* However, natural gas may not be available as a fuel for utility boilers very far into the future. For oil, the most common range today, when the combustion process has not been modified, is about 180 to 280 ppm for tangentially fired units and 300 to 700 ppm for horizontally fired units. *A realistic objective for oil-fired*

plants placed in operation by 1980, achievable by flue-gas recirculation and off-stoichiometric combustion, is about 150 to 200 ppm. For smaller furnaces or where low-nitrogen oil is available, there is a possibility of reaching this objective at an earlier date. *Control methods are not yet established for coal. The Panel recommends a review to establish realistic objectives after more data become available in the next two or three years.*

2. Both theory and practice indicate that NO_x emissions from combustion sources can be lowered by: (a) reducing the amount of oxygen present in the flame zone, as by use of staged admission of air (or off-stoichiometric combustion), and (b) reducing the peak flame temperature, as by use of flue-gas recirculation to the flame zone. *The practicality of these abatement techniques has been developed primarily in furnaces burning gas or oil. Little has been done on coal-fired units.*

3. The principal problem in reducing NO_x emissions by the use of staged combustion is to avoid the significant increase of emissions of CO, hydrocarbons, and smoke. In addition, with coal, it is important to avoid increasing the hazard of flame-outs, the rate of corrosion of boiler components caused by a reducing atmosphere, and the percentage of unburned carbon in the ash. The applicability of the above techniques to coal firing is not well understood and it will vary considerably with burner design; e.g., flue-gas recirculation may be less effective with cyclone burners than with other burner designs.

4. The amount of NO_x formed per unit quantity of heat released on combustion can vary

by a factor of about 10 depending on a number of interrelated factors: (a) the fuel (coal, oil, or gas); (b) the percentage of excess air used in combustion; and (c) the size of the furnace--as furnace sizes increase from domestic heating units to large utility boilers, the amount of NO_x formed per Btu released usually increases, probably because lower surface-to-volume ratios and increased heat-release rates per cubic foot lead to less rapid thermal quenching of the combustion process. For large utility boilers, increased furnace volume (while holding all other variables constant) will act to reduce the average temperatures and will therefore always act to reduce NO_x. However, it appears that the effect of furnace volume on NO_x formation is of secondary importance when compared with other combustion-control modifications such as off-stoichiometric combustion. This is not to say that furnace volume is insignificant. In designs in which combustion is spread out in the furnace, e.g., tangentially fired units, it seems likely that increasing furnace volume would cause a reduction in NO_x; (d) burner design--designs that produce more intense combustion and higher temperatures, e.g., cyclone burners for coal, produce considerably more NO_x than designs that allow combustion to occur out in the furnace, e.g., tangentially fired boilers. It is impractical, however, in an existing installation to replace cyclone burners with tangential burners located in the furnace corners, for this would require nearly complete rebuilding of the furnace. It is not the fact that the burners are positioned to admit fuel and air in a tangential configuration that brings about a reduction in NO formation, but rather the manner in which fuel and air are

admitted and mixed; and (e) load--as load is first reduced in any particular installation, the concentration of NO_x formed at first drops. With further reduction in load, the change in NO_x concentration is determined primarily by the degree to which increased air-fuel ratio may be required to prevent excessive carbon monoxide or smoke at lower loads.

5. Preliminary data exist regarding the relative importance of conversion to NO_x of fixed nitrogen in oil fuels. These data suggest that combustion of oil or coal under reducing (sub-stoichiometric air) conditions in a first stage helps reduce the amount of fuel nitrogen converted into NO_x or increases the conversion of NO_x to N_2 and the combustion products, but additional research is needed.

6. Presently feasible technology that can be applied to NO_x control in utility boilers varies with the fuel utilized and the nature of the installation--retrofitting an existing boiler or designing a new boiler. Furnace design (e.g., opposed vs. tangential firing), burner configurations (e.g., cyclone vs. conventional burners), and provisions for adjusting fuel and air flows and recycling combustion gases determine the degree of NO_x control achievable in an existing installation. Research, development, and design studies are needed to determine combustor configurations and designs that will facilitate complete combustion of coal and oil (avoiding carbon, hydrocarbon, and CO losses and preventing smoke and soot formation), and will at the same time minimize emission of NO_x (formed either by N_2-O_2 fixation or oxidation of nitrogen in the fuel).

7. Combined-cycle systems involving the combustion of coal or oil in combinations of gas and steam turbines are of considerable interest to utilities. Some of these may involve external coal gasification closely coupled to a turbine or boiler. NO_x emissions are expected to be low, comparable to those from natural gas, but little information is available.

8. On the basis of laboratory and pilot-scale tests, fluidized-bed-combustion boilers show promise of appreciably reduced NO_x emissions, compared with conventional coal-fired boilers. Burning of the coal is carried out at relatively low temperatures, 1400-1900° F.; tests indicate that the NO_x emissions originate almost entirely from nitrogen in the fuel. In fluidized combustors burning coal at atmospheric pressure, two-stage combustion has reduced NO_x emissions to about 70 ppm. In pressurized combustors, NO_x emissions have been reduced substantially in single-stage combustion. Fluidized-bed-combustion boilers, therefore, show excellent potential for NO_x control, and their development should be pursued.

Removal of NO_x from stack gases may offer potential for control in the future. *However, no proven process is available for substantial removal of NO_x from combustion stack gases.* Conclusions based on presently available information are:

9. Any wet scrubber system for NO_x removal will be expensive for two reasons: (a) Most of the NO_x is in the form of NO, which is relatively unreactive and insoluble. The maximum rate of absorption in an aqueous system occurs at a NO/NO_2 mole ratio of unity, which requires either (1) recycle of NO_2 and a method of generating NO_2 from the scrubbing system, in

turn requiring very high scrubbing efficiencies for substantial overall removal of NO_x, or (2) oxidation of about half of the NO to NO_2 prior to scrubbing. The rate of oxidation of NO to NO_2 is slow and decreases with increasing temperature; and (b) large vessels are required for scrubbing because of the large volumes of gas that must be handled and the necessity for low pressure drop.

10. Catalytic reduction of NO_x to N_2 by a reducing agent as a process for treating stack gases from large utility boilers requires a sulfur-resistant catalyst if coal or oil is used as a fuel. Space velocity (i.e., catalyst activity) and catalyst life also limit this approach at present. The catalytic reduction of NO_x with ammonia or other reducing agents is being studied by several groups. Information is insufficient to assess fully the potential of any catalytic reduction methods of control.

11. Decomposition of NO_x in the absence of a reducing agent requires such high temperatures, on even the best catalysts known, as to be impractical.

The following conclusions have been reached for other stationary combustion sources and for chemical manufacture:

12. Somewhere between two percent and 21 percent of the NO_x emissions from stationary sources are produced by internal-combustion engines (burning natural gas or diesel fuel, used in conjunction with pipelines and gas plants). With diesel engines, techniques such as control of fuel injection, exhaust-gas recirculation, water injection, and alteration of combustion-chamber design, are available to reduce

NO_x emissions. With gas turbines, redesign of combustors and methods of fuel injection accompanied by more fuel-lean conditions in the combustion zone should produce significant reduction in NO_x emissions.

13. More data are required on emissions from industrial process and commercial furnaces, residential furnaces and heaters, and incinerators.

14. Emissions from nitric acid plants and chemical operations may be "decolorized" (conversion of NO_2 to NO) by catalytic reduction with natural gas. A similar method can be used to reduce NO to N_2 (typically from 3,000 ppm to 100 to 500 ppm), but requires careful control. Adsorption by molecular sieves has been shown in the laboratory to produce even lower emission levels but no demonstrated commercial process is yet available. Alkaline scrubbing may be used but involves liquid-waste disposal problems.

15. In some chemical processing with nitric acid, a substantial portion of the nitrogen oxides emitted may be in the form of N_2O, which is considered to be harmless.

C. RECOMMENDATIONS

On the basis of its review and in conjunction with the above conclusions, the Panel recommends that:

1. *Combustion-modification studies be given first priority in research and development to control NO_x emissions. Studies of coal combustion are especially required. Studies of the effect of fuel nitrogen on NO_x emissions and the potential of flame-temperature-control techniques in oil and coal burning are also needed.* A substantial reduction in the amounts of NO_x

released to the atmosphere (i.e., of the order of 50 to 80 percent) will come least expensively from modifications of the combustion process rather than from scrubbing or adsorption systems to remove NO_x from stack gases.

2. Experimentation to develop firing methods for minimizing NO_x emissions be accompanied by data correlation and theoretical analyses of the data obtained in order to develop the basic understanding for configuring and designing new combustors and for choosing operational modes in a variety of applications.

3. Boiler manufacturers and utilities incorporate as much flexibility as possible in the design of new boilers to permit taking advantage in the future of increasing knowledge of the factors affecting NO_x emissions in combustion.

4. Additional work be funded on new energy-conversion concepts--such as fluidized-bed combustion, coal gasification for electric-power production, and combined-cycle gas- and steam-turbine generating plants operating in conjunction with such combustors and gasifiers--to develop their potential for reducing NO_x and other pollutants.

5. New concepts claiming potential for the economic simultaneous removal of NO_x and SO_x be evaluated carefully.

6. Evaluation of all new electric-power-generation techniques utilizing fossil fuels--including magnetohydrodynamics (MHD), fuel cells, and combined-cycle plants with fluidized-bed combustion or coal gasification--incorporating estimates of NO_x formation and the economic cost of NO_x control, begin as soon as practicable.

7. Careful consideration be given to improving present methods of sampling and analysis of NO and NO_2, particularly in the presence of other pollutants from stationary sources.

8. The potential for the generation of NO_x by such sources as stationary internal-combustion engines, industrial and commercial furnaces, residential furnaces and heaters, incinerators, electrostatic precipitators, and other high-voltage equipment needs further evaluation. If the level of emissions is significant and the effect on ambient air quality is detrimental, then control techniques should be sought.

II

INTRODUCTION

A. THE CLEAN AIR AMENDMENTS OF 1970

The increasing concern of Americans for the deterioration of the nation's air resources is reflected in the Air Quality Act of 1967 (Public Law 90-148 as amended)[2] and the Clean Air Amendments of 1970[1] (Public Law 91-604 in which Public Law 90-148 was further amended to provide for a more effective program to improve the quality of the nation's air). These acts include emission standards for existing sources that are to be enforced by the states, and performance standards for new sources that were promulgated during 1971 and are to be enforced by the Environmental Protection Agency (EPA). Responsibility for carrying out the provisions of these laws is assigned to the EPA Administrator.

Under the provisions of these laws, the EPA published in the *Federal Register*[5] guidelines to the states for preparation, adoption, and submittal of implementation plans for enforcement of national ambient air quality standards. On April 30, 1971, the EPA published the *National Primary and Secondary Ambient Air Quality Standards*.[4] National primary and secondary ambient air quality standards are those judged by the Administrator, based on the air quality criteria documents[8,9,10,11,12,13,14] published by the EPA and allowing an adequate margin of safety, as requisite to protect the public health (primary standards) and the public welfare (secondary standards) from any known or anticipated adverse effects associated with the presence of pollutants in the ambient air.

The national primary ambient air quality standards for nitrogen oxides were promulgated as follows:

The national primary and secondary ambient air quality standard for nitrogen dioxide, measured

by the reference method described, (sodium hydroxide absorption and subsequent colorimetric determination), or by an equivalent method, is: 100 micrograms per cubic meter (0.055 parts per million)--annual arithmetic mean.

Under Section 110,[1] the states have nine months to submit a plan for implementation, maintenance, and enforcement of the primary standard in each air-quality-control region and an additional nine months to submit a similar plan for secondary standards. The plans are to include a timetable for compliance within three years, and state standards may be more stringent than the federal standards. For nitrogen dioxide, the national secondary ambient-air-quality standard is the same as the primary standard.

In applying these standards it is assumed that any NO present in the air is converted to the dioxide, but the *extent to which NO is actually converted to NO_2 can vary greatly.*

Recommendations by EPA[5] to the states for possible inclusion in their implementation plans for existing sources cover emissions of nitrogen oxides from fuel-burning equipment and nitric acid manufacture. These emission standards together with standards of performance for new stationary sources[7] are as follows:

	Fuel-Burning Equipment (pounds per million Btu)			Nitric Acid Manufacture (pounds per ton)
	Gas	Oil	Coal	
Required for New Sources	0.20	0.30	0.70	3.0, 10 percent opacity
Recommended for Implementation Plans*	0.30 (175)	0.30 (230)	--- (575)	5.5 (400)

*The figures in parentheses are approximate ppm, in dry flue gas containing 3 percent oxygen.

The reasons for concern about NO_x emissions to the atmosphere are threefold: (1) Both NO and NO_2 can of themselves have adverse health effects, NO_2 being considerably more toxic than an equal concentration of NO[14]; (2) NO and NO_2 interact with hydrocarbons in the atmosphere under the influence of the ultraviolet energy of sunlight by a highly complex and only partially understood series of reactions, to generate eye irritants such as PAN (peroxyacetyl nitrate and related compounds), PBZN (peroxybenzyl nitrate and related compounds), and O_3 (ozone).[9,14] In addition, the reddish color of NO_2 (NO is colorless) can contribute to haze and decreased visibility; and (3) detrimental effects on vegetation.[14]

Following combustion, NO reacts relatively slowly with residual oxygen in the combustion equipment and in the flue gases to yield NO_2. This conversion is usually less than 10 percent because of the short residence time. Thus, NO_x released to the atmosphere from combustion processes is largely in the form of NO.[14,15] In the typical daily urban pattern, the concentration of NO and NO_2 in the atmosphere begins to increase rapidly at dawn as human activity, particularly automotive traffic, increases, the ratio of NO to NO_2 initially being very high. Under the influence of sunlight, much of the NO is converted during the day to NO_2 and concentrations of PAN, PBZN, and O_3 increase. After sunset, photochemical conversion of NO to NO_2 ceases but O_3 formed during the day continues to react with NO to form NO_2 until O_3 is depleted. In ordinary circumstances, winds and dispersion during the night reduce the concentration of pollutants to a low level and the cycle recommences the following dawn. What happens to as much as 50 percent of the nitrogen oxides that become incorporated into the photochemical complex is still undetermined, since many of the nitrogen oxide end products remain unidentified.[14]

B. ROLE OF THE ACADEMIES

The National Academy of Sciences and the National Academy of Engineering established the Environmental Studies Board in 1967 to coordinate activities of the two Academies in the environmental field. One

of the first acts of this Board was to recommend establishment of four committees on air, water, noise, and solid-waste management within the Division of Engineering of the National Research Council. These committees have an engineering orientation and are available for furnishing advice and assistance to the Congress and to agencies of the executive branch of government having responsibility for pollution abatement and control.

In June, 1969, the National Air Pollution Control Administration of the U. S. Department of Health, Education, and Welfare (now the Office of Air Programs of the EPA), requested the National Academy of Engineering to make a comprehensive review of present industry and government research, development, and demonstration programs, to include technical and economic potentials, adequacy of scope, proper integration with similar efforts, and responsiveness to national needs directed toward control of sulfur oxides effluents from stationary sources of combustion. The report on that study, *Abatement of Sulfur Oxide Emissions from Stationary Combustion Sources*,[16] was published in May, 1970.

The newly formed Office of Air Programs (OAP) of the EPA then requested the National Academy of Engineering--National Research Council to follow this study with studies of sulfur oxides emissions from industrial sources, nitrogen oxides emissions from stationary sources, and particulate emissions from stationary sources. Each study includes an assessment of the adequacy of present technology; the need for additional technology; the scope, integration, and coordination of industry and government effort; and responsiveness to the national need for control and abatement of air pollution from each of the three sources. Other similar studies are expected to follow within the next year. This report deals with the emissions of nitrogen oxides.

C. FEDERAL RESEARCH, DEVELOPMENT, AND DEMONSTRATION PLANS

The EPA has developed a five-year research and development plan for control of NO_x emissions from stationary sources.[17,18] The Panel hopes this report

will be useful to the EPA and its Office of Air Programs, other government agencies, industry, fuel suppliers, and others in planning and coordinating the research, development, and demonstration programs required to meet the national need for cleaner air.

The implementation of this plan will need to be closely coordinated with national energy policies for optimum use of resources.[19] The major emphasis will be placed on developing combustion-modification techniques that will reduce NO_x formation in coal-, oil-, and gas-fired industrial and utility boilers. Electric utility sources have received the highest priority for funding in the Development Engineering Branch of the EPA's Office of Air Programs for the following reasons: (1) Electric utilities are the largest single source of NO_x emissions; (2) the internal-combustion engines that produce the NO_x in conjunction with pipelines and gas plants can be controlled with technology developed by OAP's motor vehicle research and development program and by the automobile industry; (3) industrial, domestic, and commercial combustion sources may be controlled by selectively adapting the technology developed for electric utility sources. Combustion in furnaces produces about two-thirds of the NO_x emissions from stationary sources in the United States and will be responsible for an increasing share of this total. Combustion-modification techniques, such as low-excess-air combustion, staged combustion, flue-gas recirculation, and water or steam injection, will be investigated up to full-scale application. Basic theoretical and experimental combustion studies will be performed through fiscal year 1975 in support of the large-scale work.

The complex nature of control of NO_x, SO_2, and other pollutants from coal combustion, and to a lesser extent from the combustion of other fuels, fully justifies serious federal attention and support for development of processes for production of "clean" fuels by such methods as fluidized bed gasification, coal gasification, coal liquefaction, and processing of our vast deposits of oil shale. This requires careful planning and coordination by OAP with other federal agencies especially the Office of Coal Research and

the Bureau of Mines. Projections for use of fuel resources[20] should include considerations such as burning low-sulfur fuel in commercial and industrial boilers and higher sulfur fuels in electric utility boilers.

The second area of emphasis for the next five years will involve the development of combustion flue-gas treatment processes to remove nitrogen oxides once they have been formed. The control of NO_x emissions by combustion modification may be limited by special process requirements for very high temperatures, limited space restrictions, or possibly the inherent fixed-nitrogen content of the fuel. Flue-gas treatment techniques, including selective catalytic reduction, aqueous alkaline scrubbing, and other selective adsorption and absorption techniques, will be scheduled for research and development.

The third area of emphasis through fiscal year 1975 will be the development of needed control technology for processes that manufacture or use nitric acid. Such processes emit small quantities but high concentrations of nitrogen oxides. Limited control technology is already available, but OAP support may be necessary to encourage further improvements in such techniques as catalytic reduction, alkaline scrubbing, and adsorption. This area may profit from developments in combustion flue-gas cleaning.

The EPA budget for stationary-source nitrogen oxides control in FY 1971 was just over $1 million. In FY 1972 it is $1.5 million; it is projected to be $4.2 million in FY 1973, $8.0 million in FY 1974, $12.0 million in FY 1975, $23.0 million in FY 1976, and $17.0 million in FY 1977. Funding is then expected to decrease sharply. *The Panel concludes that the research and development plans and the funding levels proposed by EPA are prudent and are required for achievement of national goals as presently defined.*

Most of the information on health hazards associated with NO_x, on ambient air and emission standards, on combustion-modification methods, and on progress in control of NO_x from mobile sources has been

developed very recently, much of it during the course of the Panel meetings. The Panel believes it to be desirable to issue its findings now even though the rapidly developing understanding of this problem may cause some revisions in judgment in the near future, particularly with respect to those sources for which standards are soon to be established. The Panel's assessment was completed before all the background information was available from EPA on the proposed new source performance standards.[6,7]

III

SOURCES OF NITROGEN OXIDES

Of the various oxides of nitrogen, the most important as air pollutants are nitric oxide (NO) and nitrogen dioxide (NO_2), generally grouped together and referred to as nitrogen oxides (NO_x). Other oxides of nitrogen, N_2O_3, N_2O_4, N_2O_5, and NO_3 are present in very low concentrations, and although they may participate in photochemical reactions they can be neglected for present purposes. Nitrous oxide or laughing gas (N_2O) is present in the atmosphere in concentrations of about 450 $\mu g/m^3$ (0.25 ppm)[14] but is regarded as being harmless physiologically, and there is no evidence that it participates in photochemical reactions in the lower atmosphere.[14]

Most NO_x is produced biologically; fixation by lightning seems to be relatively unimportant.[15] Natural sources produce on the order of 50×10^7 tons per year (about 90 percent of the total) of NO_x, worldwide, while man-made sources emit about 5×10^7 tons per year (about 10 percent of the total). Naturally occurring sources of NO_x have been found to cause nonurban concentrations, usually less than 10 $\mu g/m^3$. However, urban concentrations are generally 10 to 100 times higher, which indicates the importance of the man-made sources even though, overall, they are a small fraction of the natural sources. Nationwide, the man-made sources that are the major cause of NO_x emissions are fuel combustion in furnaces and in engines.[15,21] Industrial chemical processes are responsible for high, localized emissions, but are not significant on a large scale. A summary of estimated man-made NO_x emissions in the United States in 1969 is given in Table 1 and a breakdown of estimated emissions from stationary sources, 1968, is given in Table 2.

About 53 percent of the total NO_x emissions in the United States are from stationary sources. The largest contributions are from fossil-fuel-fired boilers for electric utilities and from industrial furnaces. At the 1970 level of control, NO_x emissions from

TABLE 1

SUMMARY OF ESTIMATED MAN-MADE NITROGEN OXIDES EMISSIONS IN THE UNITED STATES, 1969
(Environmental Protection Agency, May 1971)

Source		10^6 Tons/Year
Transportation		11.1
Motor vehicles, gasoline	7.6	
Motor vehicles, diesel	1.1	
Aircraft	0.3	
Railroads	0.1	
Vessels	0.2	
Nonhighway	1.8	
Fuel Combustion in Stationary Sources		10.0
Coal	3.8	
Fuel oil	1.3	
Natural gas	4.7	
Wood	0.2	
Industrial Process		0.2
Solid waste		0.4
Miscellaneous		2.0
Forest fires	1.6	
Structural fires	-	
Coal refuse	0.1	
Agricultural	0.3	
TOTAL		23.7

TABLE 2

BREAKDOWN OF ESTIMATED NO_x EMISSIONS FROM STATIONARY SOURCES IN THE UNITED STATES, 1968
(Environmental Protection Agency, May 1971)

Source	Percentage of Total
Electric utility boilers	38
Industrial combustion	29
Pipelines and gas plants	21*
Domestic and commercial	10
Noncombustion sources	2

*Estimates range from 2 percent to 21 percent.
(See remarks on page 39.)

stationary sources would approximately double by the year 2000.[17]

NO_x emissions from stationary sources in the United States result primarily from the combustion of fossil fuels in boilers, furnaces, and stationary internal-combustion engines. The bulk of the NO_x emitted by industrial sources comes from steam boilers and process heaters, with smaller amounts from internal-combustion engines, boilers burning waste-fuel gases, catalytic cracking regenerators, metallurgical ovens, furnaces, and kilns. On the other hand, emissions from pipeline and gas plant operations, result primarily from the use of internal-combustion engines to drive pumps and compressors, and to a lesser extent from process heaters and boilers. Domestic and commercial sources include incinerators, space heaters, water heaters, ranges, and clothes dryers. Essentially all the NO_x emitted by noncombustion sources comes from the manufacture or use of nitric acid.

NO_x distribution is closely related to population distribution; over 60 percent of the NO_x emissions in the United States occur in urban areas. The relative contributions from stationary and mobile sources vary substantially from city to city and the contribution at ground level presumably comes proportionately more from mobile sources than from stack emissions. Stack height and meteorological factors also affect the relative contributions. NO_x has a residence time in the atmosphere of three to four days. Thus, pollution from NO_x is a regional rather than a global problem.

Almost all NO_x emissions arise from combustion processes. The nitrogen oxides are formed during combustion by chemical combination of oxygen and nitrogen in the air (fixation), and by oxidation of some of the nitrogen combined with organic substances in the fuel. Only a small fraction of the nitrogen in the air passing through a furnace or an engine is converted to NO_x. Likewise, only a portion of the nitrogen in the fuel is converted to NO_x. However, the total tonnage of NO_x emitted, if it were converted to nitric

acid, is 10 times the U.S. production of this chemical. Coal varies between about 1.0 and 1.5 percent by weight and fuel oil between about 0.02 and 1.2 percent by weight in the amount of combined nitrogen they contain. Natural gas contains no significant amount.

Unlike emissions of SO_x, which are directly proportional to the sulfur content of the fuel, NO_x is formed in conventional combustion processes largely by fixation of nitrogen and oxygen from the atmosphere at the high temperatures existing during combustion. Under conventional combustion conditions a smaller contribution is from organo-nitrogen compounds in the fuel.

The major factors influencing NO_x emissions from combustion processes are: the percent of excess air; mixing; heat release and removal rates; fuel type; and fuel composition.[17,48] These factors provide a basis for modifying combustion techniques of NO_x control. Modification of operating conditions include: operation at reduced load; low excess-air firing; staged or off-stoichiometric combustion; flue-gas recirculation; steam or water injection; reduced air preheat; and combinations of these methods. The NO_x level can also be reduced by changes in design such as: altering burner-design configuration, location, and spacing; use of tangential firing; and, potentially, fluidized-bed combustion.

The meteorological aspects of the NO_x pollution problem can be considered in three general areas, which are not necessarily mutually exclusive in all respects:[14]

1. The transport and dispersion of nitrogen oxides--of particular importance in urban areas.

2. The relationship between concentrations of oxides of nitrogen and meteorological factors, especially in relation to transformation processes in the atmosphere.

3. The effects of NO_2 concentrations on visibility and sky coloration.

Studies in Los Angeles give the following results for the relationships between oxides of nitrogen and meteorological factors:

1. A correlation was found between the "hourly average concentrations" of hydrocarbons (HC) and NO_x.

2. The HC/NO_x and HC/CO ratios indicate that NO_x concentration is a complex function of temperature.

3. The maximum daily NO_x concentration is inversely related to inversion height and wind speed and is independent of light intensity.

4. The maximum daily oxidant concentration is a function of the square root of light intensity.

Similar studies in Cincinnati[22] generally confirm these and other observations. For example: HC, NO, and CO reach their peak concentrations at about 8:00 a.m., NO_2 about 9:30 a.m., while O_3 increases monotonically through the period. The ratios CO/NO_2, CO/NO, and NO_2/NO increase rapidly on warm days, whereas the NO_2 peak occurs later on cold days. However, to a considerable extent each city is unique. The relative ratios and quantities of pollutants emitted and their effect on ambient conditions vary greatly because of differences in fuels burned, types of boilers and furnaces, nature of industry and of transportation, and meteorological conditions. Although nationwide emission standards are being established, it is important that better models be developed for individual cities and local air-quality regions with respect to the sources and fate of air pollutants, so that local decisions can reflect optimum strategies both for continuous control and for action under emergency conditions.

The national ambient air quality standards for NO_x rest very heavily on a series of studies in Chattanooga, Tennessee, on school children.[3,4,5,6,7,22,23] These standards call for a mean concentration of NO_2 not exceeding 100 $\mu g/m^3$ during the year. It is not clear, however, that these studies provide a sufficiently broad data base for firmly establishing ambient air standards for NO_x. It involved primarily children, and the majority of the NO_x was produced by a single source. The fluctuations of NO_x concentrations around mean values (including relatively higher peak concentrations) are wider with a single source than with multiple sources. Health and environment effects may be more attributable to peak concentrations than to mean values. The current ambient-air standard for NO_x is probably being exceeded in portions of major cities of the United States; therefore, additional data should be sought to confirm this standard. The current view of the EPA appears justified in that it is reasonable and prudent when promulgating air quality standards, to give consideration to requirements for a margin of safety that would take into account possible effects on health, vegetation, and materials that might occur. However, the Panel does not feel competent to evaluate the standard itself, from the viewpoint of hazard to health and welfare.

A national strategy may be needed to achieve substantial reduction of NO_x levels in urban areas. Ground-level concentrations appear to be related to mobile sources and domestic heating more than to large single sources that discharge through tall stacks. A program of monitoring, modeling, and land-use planning will need to be developed for each urban area in order to obtain acceptable air quality with respect to nitrogen oxides and other pollutants.

In 1970, electric utilities placed new orders for electric generating equipment of about 30 million kilowatts capacity to burn fossil fuels and of about 15 million kilowatts capacity using nuclear fuel. For various reasons it is expected that this ratio of two to one for new equipment using fossil and nuclear fuels will be maintained for the next several years, thus ensuring that the generation of NO_x will be a continuing significant problem. Electric utilities in the

past have been dependent upon equipment manufacturers for research and development. Control of NO_x and other pollutants may require them to engage in research and development to solve their individual problems. Encouragement to do so will depend heavily on the attitudes of the regulatory agencies, which must approve the rates charged by the utilities for electrical energy.

Fuel use involves many factors. One has been the increasing emphasis on air-pollution control and the substitution of low-sulfur oils for some of the high-sulfur coals. There has also been a balancing of installed equipment in utilities systems to use low-capital-cost, peaking-type (gas or oil) equipment to supplement the base-loaded nuclear equipment as it is added to a system, so some of the growth in oil firing during the recent past was of the peaking variety, and some of it was the substitution of oil for coal (especially along the Eastern Seaboard) where oil can often be brought directly into the power plant. Considerations of fuel availability and strategies for NO_x control could lead to conversion of smaller sources to gas. This and other factors are expected to spur research and development of coal gasification, fluidized-bed combustion, and changes in combustor design. It is generally agreed that at present the state of the art for gas and oil firing permits the concentration of NO in the stack gas to be reduced to somewhere in the range of 150 to 250 ppm* on large units employing one or more of the latest combustion modifications.

The importance of air-pollution control is clear. However, an economic price must be paid and the cost of reduction of any pollutant, per unit quantity of

*The concentration of NO_x is obviously affected by the amount of excess air used. To have a common basis for comparison it is customary to calculate the NO_x concentration that would exist on a water-free basis if the oxygen concentration in the exit gases were 3 percent. For regulatory and other purposes, it may be desirable to express NO_x emissions in terms of quantity produced per Btu released or kilowatt-hour generated.

that pollutant, increases the higher the percentage removal specified. For lower concentration streams the cost per unit removal also increases with the total volume processed. These economic costs can be major and will ultimately be borne by the economy as a whole. They should not be glossed over in the nation's drive toward cleaner air. For those pollutants that already are or may become global problems, it is important that global standards be adopted.

IV

FORMATION AND CONTROL OF EMISSIONS FROM COMBUSTION SOURCES

A. EQUILIBRIUM AND KINETICS

It appears that most of the NO is formed by the high-temperature reaction of molecular nitrogen and oxygen present in the combustion air via the following chain-reaction mechanism:[24]

$$O_2 \leftrightarrows O\cdot + O\cdot$$

$$O\cdot + N_2 \leftrightarrows NO + N\cdot$$

$$N\cdot + O_2 \leftrightarrows NO + O\cdot$$

Some of the NO_x doubtless also results from the oxidation of organically bound nitrogen in the fuel.

The fixation of nitrogen and oxygen is thus represented by the overall reaction:

$$N_2 + O_2 = 2NO$$

The rate and extent of this reaction increases very rapidly with increased temperature. The thermodynamic equilibrium constant is given by:[17]

$$K = 21.9 \exp(-43{,}400/RT)$$

The formation of NO is favored at high temperatures. Equilibrium concentrations of NO at flame temperatures are of the order of 3,000 ppm, while the NO_2 levels are negligible.

The concentrations of NO actually found in the stack gases are usually much less than the equilibrium concentration that could exist at the flame temperature in the furnace but much greater than that corresponding to the temperature of the gases leaving the furnace. It seems likely, then, that the NO concentration is determined by the time-temperature-composition history of the gases as they move through a

furnace or other combustion system. This theory is supported by theoretical chemical kinetic calculations and experimental studies on premixed flames that show that the NO is formed after most of the fuel combustion has been completed. These experiments also indicate that the NO-formation process is strongly temperature-dependent (the most rapid rates occurring at peak combustion temperatures) and that little, if any, NO decomposition occurs. It is therefore concluded that the amount of NO emitted in gas- and oil-fired systems is essentially determined by the characteristics of the forward reaction forming NO. For coal firing, however, the amount of NO in the gases may go through a maximum and decrease as the gases cool. It is possible that the ash may have a catalytic effect in decomposing some of the NO initially formed at the higher temperatures. Although NO_2 is favored thermodynamically over NO at lower temperatures, relatively little is formed during the rapid cooling of combustion gases in passing through a furnace and in dispersion into the atmosphere. About 90 to 95 percent of the NO_x dispersed into the atmosphere is in the form of NO.

Fundamental differences remain in understanding just how NO is formed in a furnace. One viewpoint applicable to one-dimensional premixed air-fuel systems, which lends itself readily to quantitative modeling, regards most of the NO as being formed after much of the fuel combustion has been completed. The NO concentration is thus regarded as being determined by the time-temperature-composition history of the gases as they flow through a furnace or other combustion system. Another viewpoint applicable particularly to gas fuel, but also to some extent to oil and coal, considers most of the NO in a furnace (which is not operated to minimize NO formation) as being formed in the primary combustion zone within a few feet of the burner. NO is visualized as being formed as pockets of fuel react in the primary zone near the burners at near-stoichiometric conditions--conditions essentially unrelated to the burner air-fuel ratio. The burner air-fuel ratio, rather, determines the number of pockets or eddies that react at near-stoichiometric conditions, each reaching peak temperature and forming high NO. The amount of NO formed in

each pocket depends upon the temperature-concentration history of the products in each pocket as it passes out into the bulk-gas region, mixing with air and products of combustion as it goes. Firing fuel-rich may be considered as reducing the number of pockets reacting in the primary zone, thus reducing NO formation.

The amount of NO_x formed in boilers can, in principle, be calculated by solving the coupled set of three-dimensional differential equations describing the transfer of mass, momentum, energy, and species. Such a solution would include the effects of flow pattern, interaction between flow patterns, molecular and turbulent diffusion, chemical kinetics, two-phase flow, and radiation-heat transfer. However, due to basic uncertainties concerning how to describe such phenomena as turbulence and to the complexity of solving these equations, the mathematical models are necessarily a simplification of the real situation. They have made valuable contributions to understanding the basic processes relating to NO_x formation and thus to suggesting ways of modifying boilers for lower NO_x production. They cannot, at present, accurately predict the change in NO_x formation that will be caused by a given modification. These mathematical models are undergoing constant refinement as their predictions are tested against data and as the effects of various simplifying assumptions become clearer. They may be used as aids to the planning of laboratory and field testing of combustion-modification techniques, in the evaluation of data from such testing, and in the design of new boilers and modification of old ones to achieve minimum NO_x.

Experimentation to develop new firing methods for minimizing NO_x emissions should be accompanied by theoretical analyses of the data obtained in order to develop mathematical models of general usefulness for prediction.

B. FACTORS AFFECTING UTILITY BOILER EMISSIONS

The major factors affecting the formation of nitrogen oxides in combustion processes, based on both theory and practice, are:

1. *Combustion temperature.* NO-formation equilibrium and kinetics are extremely dependent upon peak combustion temperatures, with higher peak temperatures favoring higher emissions.

2. *Availability of combustion air.* NO formation is dependent upon the availability of air for the "fixation" reaction shown.

3. *Mixing of fuel, air, and combustion products.* Internal recirculation or "backmixing" of combustion products into the combustion zone dilutes the fuel and air, lowers the flame temperature, and thereby reduces NO_x emissions. Distribution of the fuel and air so as to achieve most of the combustion under fuel-rich conditions and the rest under fuel-lean (excess air) conditions also reduces NO_x emissions. Slow diffusion of the fuel and air streams can also accomplish this objective.

4. *Heat release and removal.* Low heat-release rates and high heat-removal rates reduce NO formation, because lower peak temperatures and shorter residence times at high temperatures are achieved.

5. *Fuel type.* On an equivalent heat-input basis, using modified combustion techniques, coal firing usually emits the most NO_x; oil emits less; and gas the least.

NO_x emissions from combustion sources can be reduced by two major techniques--combustion modification and flue-gas treatment. Combustion-modification techniques presently appear to be the quickest and most economical methods of accomplishing major reduction of NO_x emissions. Those techniques that have been conceived (some have been tried) are low-excess-air operation, staged or off-stoichiometric combustion, flue-gas recirculation, reduced air preheat, steam or water injection, or a combination of these techniques.

Low-excess-air combustion reduces NO_x emissions because the availability of oxygen is reduced. Staged or off-stoichiometric combustion is the technique

of introducing combustion air in stages so that the partially burned fuel and combustion products are permitted to cool before the completion of combustion; thus, the simultaneous exposure of the nitrogen to oxygen and to high temperatures is avoided. Much of the combustion occurs under fuel-rich conditions.

External recirculation of flue gas into the combustion zone, like internal "backmixing," dilutes the fuel and air, lowers the flame temperature, and thereby reduces NO_x emissions. Injection of steam or water into the combustion zone or the reduction of air preheat also has the same effect. Flue-gas recirculation has been practiced for many years as a method of adjusting temperature distribution in a boiler, but this has usually not involved recirculation back to the burner region, which is required for optimum NO_x control.

Low-excess-air staged-combustion and gas-recirculation techniques have been used successfully by some California utility companies firing gas[25] and applicability to oil firing is being investigated by these same companies.[26] However, very little work has been done to apply these and other combustion-modification techniques to coal-fired units. The alteration of firing procedures may also affect the heat-transfer characteristics of a boiler and hence the thermal efficiency, consequences that must be kept in mind in searching for suitable modifications.

Flue-gas treatment, the second technique, is the removal or decomposition of the NO_x after it has been formed and is described in more detail in Chapter V of this report. The most promising candidates for further development are aqueous scrubbing systems using alkaline solutions or concentrated sulfuric acid. To be effective, however, the NO_x must be scrubbed out in equimolar concentrations of NO and NO_2. Since less than 10 percent of the NO_x present in stack gases is NO_2 and the remainder is NO, some method of equalizing the concentrations is needed. The best method appears to be the recycle of NO_2, since catalytic oxidation of NO to NO_2 in the main flue-gas stream is both too expensive and too slow. Other flue-gas treatment

techniques that are candidates for development are catalytic reduction, adsorption by solids, and catalytic decomposition, the last being probably the least promising.

The amount of NO_x formed per unit quantity of heat released on uncontrolled combustion can vary by a factor of about 10 depending on a number of interrelated considerations:

1. *The fuel (coal, oil, or gas).*

2. *The percent excess air used in combustion.*

3. *The size of the furnace.* As furnace sizes increase from domestic heating units to large utility boilers, the amount of NO_x formed per Btu released usually increases, probably because of lower surface-to-volume ratios, which lead to less rapid thermal quenching of the combustion process. For large utility boilers, increased furnace volume (while holding all other variables constant) will act to reduce the average temperatures and will therefore always act to reduce NO_x. However, it appears that the effect of furnace volume on NO_x formation is of secondary importance when compared to other combustion-control modifications such as off-stoichiometric combustion. This is not to say that furnace volume is insignificant. In designs in which combustion is spread out in the furnace (e.g., tangentially fired units) it seems likely that increasing the furnace volume would cause a reduction in NO_x.

4. *Burner design.* Designs that produce more intense combustion and higher temperatures, (e.g., cyclone burners for coal) produce considerably more NO_x than designs that allow combustion to occur out in the furnace, (e.g., tangentially fired boilers). It is impractical, however, in an existing installation to replace cyclone burners with tangential burners located in the furnace corners, for this would require nearly complete rebuilding of the furnace. It is not the fact that the burners are positioned to admit fuel and air in a tangential configuration that brings about a reduction in NO formation, but rather the manner in

which fuel and air are admitted and mixed. It may be possible in some instances to incorporate the mixing features of tangential burners into wall-fired burner designs as more is learned of these features. In other instances where cyclone burners are required because of the specific type of coal used, this may not be possible.

5. *Load.* As load is first reduced in any particular installation, the concentration of NO_x formed at first drops. With further reduction in load, the change in NO_x concentration is determined primarily by the degree to which increased air-fuel ratio may be required to prevent excessive carbon monoxide or smoke at lower loads.

Certain residual fuel oils, e.g., those from California and Venezuela, have a relatively high content of organo-sulfur and organo-nitrogen compounds. Fuel oils from California are especially high in organo-nitrogen compounds. The nitrogen content is usually lower than the sulfur content in oils that have not been desulfurized. The range of the nitrogen in California residual fuel oil is about 0.3 to 1.0 percent, and for a Venezuelan fuel oil, from 0.1 to about 0.5 percent. Desulfurization of fuel oil also removes some of the nitrogen and the fraction of nitrogen removed increases as operating conditions are altered to increase sulfur removal. With firing of residual fuel oil in conventional equipment, as a rough guide, perhaps about a third of the fixed nitrogen is emitted as NO_x.

Many coals contain substantial quantities of fixed nitrogen. One percent nitrogen in coal would result in about 1,500 ppm of NO_x in the stack gases (stoichiometric conditions) if it were all converted to NO_x. Even though much is in fact released in the form of N_2, the remainder can be a significant contribution to total NO_x emissions.

Preliminary data exist regarding the relative importance of conversion of fixed nitrogen in oil fuels to NO_x. These data suggest that combustion of oil or coal under reducing (sub-stoichiometric air) conditions in a first stage helps reduce the amount of

fuel nitrogen converted into NOx or increases the conversion of NO_x to N_2 and combustion products, but additional work is needed.

Boiler manufacturers are being asked to provide guarantees on the maximum amount of NO_x that will be emitted. *Of the three fuels used in firing, gas, oil, and coal, gas allows the most precise control in the attainment of the lowest levels of NO_x.* The term "coal" covers a variety of types of solid fuels varying greatly in their combustion characteristics, and therefore a substantial variety of boiler and burner designs are required to burn these various types satisfactorily. *Present emission levels from coal firing vary greatly. Of the three fuels, least is known about coal relative to minimizing NO_x formation from combustion.* The Panel is aware of only three instances in which coal-fired utility boilers have been operated with staged admission of air or two-stage combustion. The results were encouraging and need to be extended.

A long lead time is required for the sequence of research, development, design, construction, and operation. *A realistic goal for 1980 for firing of natural gas in new plants is a reduction in NO_x concentration to about 100 ppm from present-day values, which are about 350 to 400 ppm uncontrolled, but range as high as 1,400 ppm.* However, natural gas may not be available as a fuel for utility boilers very far into the future. *For oil, the most common range today when the combustion process has not been modified is about 180 to 280 ppm for tangentially fired units and 300 to 700 ppm for horizontally fired units. A realistic goal for 1980 in new plants, achievable by flue-gas recirculation and/or staged combustion, is 150 to 200 ppm.*

Both theory and practice indicate that NO_x emissions from combustion sources are lowered by: (a) reducing the amount of oxygen present in the flame zone, as by use of staged or off-stoichiometric combustion admission of air, and (b) reducing the peak flame temperature, as by use of flue-gas recirculation. The practicality of these techniques has been tested primarily in furnaces burning gas or oil. Limited data

make it appear that flame-temperature-control techniques may not be as beneficial with oil fuel as with gaseous fuel. Little has been done on coal-fired units.

The principal problem in reducing NO_x emissions by the use of staged and off-stoichiometric combustion is achieving the reduction without significantly increasing emissions of CO, hydrocarbons and smoke; or with coal, increasing the hazard from flameouts or increasing unburned carbon in the ash. The applicability of these techniques to coal firing may vary considerably with the slagging characteristics of the coal and with burner design; e.g., gas recirculation may be less effective with cyclone burners than with other burner designs, if gas is recirculated into the furnace, because most of the combustion occurs within the cyclone burners. However, if a modified operation (including burner redesign) could be established for recirculation directly into the cyclone, this approach might be useful.

Costs for boiler modifications are quite varied. For example, as of March 1971, fossil-fueled power plant costs range from $100 to $350 per kilowatt of capacity. The boiler alone costs $35 to $65 per kilowatt. For large new gas-fired units the addition of flue-gas recirculation (to the windbox) adds about $2.65 per kilowatt. The cost of over-firing or two-staging would add about $0.15 to $0.25 more. For oil-fired units some recirculation is generally part of the basic design; to modify it to recirculate to the windbox adds about $1.50; over-fire air costs an additional $3.50; staging costs an additional $0.25 to $0.50. Oversizing a boiler by 50 percent will cost an additional $3.75 to $7.50 per kilowatt depending on the fuel used. The potential benefits of oversized boilers to obtain reduction of NO appear to be small in comparison with other methods of NO control. Retrofitting of existing units for gas recirculation or redistribution of air would be much more expensive than the costs cited above.

The definition of what constitutes a new plant is difficult but important, since the first set of emission standards are specified to apply to "new

plants." For nitrogen oxides particularly, most of the control methods now available depend on boiler modifications, so it would appear that once the purchaser has specified the boiler, the plant can no longer be termed new. There is about a seven-year period between initial commitment by the utility and the operation of a new power plant. The first set of ambient air standards that will become applicable in 1975 is based, first, on what is desirable, and second, on what is achievable.

With respect to utility boilers, presently feasible technology for control of NO_x varies greatly with the fuel used, the nature of the burners (e.g., cyclone versus tangential burners), and the age of the unit. Boiler manufacturers and utilities should incorporate as much flexibility as possible in the design of new boilers to be able to take advantage in the future of the growing knowledge of the factors affecting NO_x emissions in combustion. A long time scale is involved between design and actual operation of a boiler which tests out the effect of substantial modifications. Because boilers are highly complex, only a two-to-one to four-to-one extrapolation on size in construction can be justified and much testing must be done on full-size units. Thus the testing of new concepts is a lengthy and expensive procedure.

C. FLUIDIZED-BED COMBUSTION

Coal (or oil or gas) can be completely burned at 1,400° F. to 1,800° F. within a bed of limestone, dolomite, ash, or inert particles suspended by the flowing combustion air and products. Such a system promotes high volumetric heat release, and high heat-transfer rates to steam tubes submerged in the particle bed. Boilers can thus be made smaller and cheaper. Such boilers may also reduce atmospheric pollution. The limestone or dolomite absorbs most of the sulfur content of the fuel and the production of NO_x is reduced due to the low combustion temperature in the bed. The quantity of fine particulates produced is also less because typically the coal is in the size of 100 mesh to 1/4-inch material in contrast to 200 mesh in pulverized coal burners.

Research and development in fluidized-bed combustion was begun by the British Central Electricity Generating Board and has been continued by the National Coal Board (NCB) in Great Britain and by the U.S. Department of the Interior's Office of Coal Research (OCR), and more recently by contractors of the OAP of the EPA in the United States. Steam-generating pilot plants have been built and operated at both atmospheric and superatmospheric pressures.

Fluidized-bed boilers can be operated at atmospheric pressure as a replacement for conventional pulverized fuel boilers or at pressure (8 to 30 atmospheres) with air compressors and gas turbines in a combined-cycle power plant. The British NCB and Westinghouse, under contract to OAP, have produced boiler designs and have estimated the performance of fluidized-bed boilers in utility power plants. Estimates indicate that the cost for power plants based on pressurized fluidized-bed boilers will be 20 to 30 percent less than for conventional plants with stack-gas scrubbing systems (for removal of SO_2). Six contractors to OAP have also demonstrated the air-pollution-control potential of such devices.

Fluidized-bed combustion in the past has been used for coal, oil, gas, or waste material. Currently, paper-mill wastes are burned in fluidized-bed combustors, as are oily wastes from refineries, sewage sludge, and trash. NO_x formation in fluidized-bed combustion can be reduced to below that in conventional furnaces. The equilibrium concentration of NO with 10 percent excess air at temperatures between 1,400° F. and 1,900° F. is about 30 to 70 ppm. It has been generally observed that burning coarse coal containing approximately 1.0 to 1.4 percent fixed nitrogen in fluidized beds results in 250 to 500 ppm of NO_x in the off-gases. However, the Argonne Laboratory has observed that, with use of 80 percent of stoichiometric air, the NO_x concentration is only 50 to 70 ppm. The NCB, under contract to OAP, has carried out fluidized-bed combustion in tests at five atmospheres in which NO_x emissions have ranged from 50 to 150 ppm. It appears that the lower the SO_2 content, the higher the NO_x content of the flue gases,

i.e., that some reaction occurs between limestone, SO_2, and NO_x in a fluidized bed to help remove NO_x.

On the basis of laboratory and small-scale work, pressurized fluid-bed boilers show promise of having advantages over conventional coal-fired boilers. Combustion occurs at substantially lower temperatures than in ordinary combustion processes and the NO_x formed comes largely from fixed nitrogen in the fuel. NO_x emissions may be somewhat reduced by additives to the bed. "Two-stage" fluid-bed combustion (reducing conditions in the bed, followed by secondary air injection) can reduce NO_x to low levels, according to laboratory data. Pressurization also appears to reduce NO_x emissions from fluidized-bed combustion of coal to a low level.

D. OTHER COMBUSTION PROCESSES

1. Gas Turbines

Stationary gas turbines and diesel engines are sources of significant NO_x emissions. Some of the simplest approaches to control of emissions from diesel engines are: retard the timing to the range in which both the smoke and NO_x emissions decrease; and use a larger period of injection for the same amount of fuel so that the rate of heat release in the cylinder is decreased. Rate of injection and retarded timing tend to be more of a problem on high-swirl chambers and less of a problem on quiescent chambers. Another method is staged injection--pilot injection followed by main injection. These techniques have been shown to produce a fairly high reduction in NO_x from existing engines, although there is a penalty in some loss in thermal efficiency. Water injected into the intake manifold or emulsified in the fuel for diesel engines has also proven successful, as has exhaust-gas recirculation and lowering of the compression ratio.

On turbines the techniques of exhaust recirculation, water injection, and combustor redesign are also applicable. A combination of fuel-injection techniques and lean operation appears to offer the most

promise for reducing NO_x from gas turbines.[11,12] This involves changing the mixing patterns, adding excess air at various points along the length of the combustor, and recirculation of a portion of the exhaust gases. Various fuel additives may possibly reduce emissions, but no demonstrated technology or promising research data exist.

Approximately 20 percent of the capacity of the electrical generating additions in 1970 were in the form of gas turbines for peaking power. In 1985, perhaps as much as 30 percent of the capacity of the additions may be in the form of gas turbines, both for supplying peaking power and for use in combined cycles. The combined cycles would be for intermediate generation, 40-to-60-percent load factor. A variety of combined-cycle plants can be visualized but typically a portion of the power is generated by a gas turbine and the remainder by a steam turbine. The outlet temperature from the combustor of a gas turbine is typically 1,600° F. and will probably be 1,800° F. in a few years. A rise to 2,000° F. or 2,200° F. can be projected as the years pass and higher efficiencies are sought and technology becomes available. An 1,800° F. outlet temperature gives approximately 170*[27] ppm of NO_x with 250-to-300-percent excess air, which is equivalent to 570 ppm (dry, 3 percent O_2). These gas-turbine NO_x emissions were measured while burning jet fuel; the amount of NO_x produced while burning low-Btu gas produced by coal gasification is unknown and needs to be determined. With gas turbines, more of the NO_x produced is in the form of NO_2 because of the high excess air at which they operate, and they can show a noticeable plume with about 9 or 10 ppm NO_2.

Estimates of NO_x emissions produced by internal-combustion engines, either reciprocating or turbines, used with pipelines and gas plants vary widely. Estimates range from 21 percent to 2 percent of the total NO_x emissions from stationary sources.

*Heavy-duty gas turbine at full load (19 megawatts) using jet fuel.[27]

The resolution of this discrepancy requires further investigation. With *diesel engines*, a variety of techniques, such as control of fuel injection, exhaust-gas recirculation, water injection, and alteration of combustion-chamber design, are available to reduce NO_x emissions to substantially below the uncontrolled level. Exhaust-gas recirculation and water injection are also potentially applicable to stationary engines other than diesels. *Catalytic mufflers* developed for control of emissions from vehicles may also be applicable to stationary engines. Indeed, control of emissions from stationary engines should be easier than with mobile engines. They usually run continuously at constant load, and space and weight limitations are less. With *gas turbines*, redesign of combustors and methods of fuel injection accompanied by more fuel-lean conditions in the combustion zone should produce significant reduction in NO_x emissions.

Burning coal in a reducing atmosphere (e.g., 60 percent theoretical air) with added water or steam generates a low-Btu gas, which can be burned in a boiler or gas-turbine combustor. This process, called gasification, reduces the quantity of NO_x formed in steam or power generation much as does two-stage combustion of natural gas. Coal and/or oil gasification provides interesting possibilities not only for reducing NO_x but also for removing particulates and sulfur in the form of hydrogen sulfide. The volume of fuel gas, usually produced at 10-30 atmospheres pressure is much less than that of the stack gases, and thus particulate and sulfur removal are simplified. Many different gasification processes and power-generation cycles have been suggested. The supercharged combined gas turbine-steam turbine and magnetohydrodynamic (MHD) cycles have the potential of further improving the heat efficiency of the entire cycle and reducing power-plant capital costs, whereas other systems for removing NO_x and SO_x may offer only air-pollution control.

Combined-cycle systems involving the combustion of coal or oil in a combination of steam turbines and gas turbines are of considerable interest to utilities. Some of these may involve external coal-gasifica-

tion processes close-coupled to a turbine or boiler. NO_x emissions are expected to be low, but little information is available.

Reliable commercial methods for gasification of coal to produce both a synthetic natural gas to supplement existing natural-gas supplies, and a gas of less than pipeline quality to be used as an electric-utility fuel and probably having other commercial, industrial, and residential uses, are of considerable interest. Fuel costs will be higher than projected gas prices or the cost of the same amount of energy from coal. However, the advantages of an environmentally acceptable "clean" fuel and the reduced capital cost and increased efficiency of combined-cycle plants may outweigh the higher fuel costs for power generation.

Magnetohydrodynamic generation of electricity uses high pressure and temperature combustion with seeding of potassium or cesium to raise the gas-ionization level. The gas is then passed through a magnetic field to generate direct-current electricity. The hot exhaust gas is sent to a boiler or turbine for additional electricity generation so that the complete system is very efficient. The combustion occurs at such high temperatures that significant quantities of NO_x are produced.

Any economic evaluation of MHD as a future power source should incorporate as a part of the analysis the economic costs of control of the large amounts of NO_x that will undoubtedly be formed. If flue-gas recovery methods for NO_x were developed in conjunction with MHD, they could have a major impact on nitric acid (HNO_3) manufacture. Pollution-control costs have a significant influence on the economics of this method of energy generation.

2. Domestic Heaters

Since domestic heaters are small and involve a great diversity of equipment, no single solution is universally applicable.[28] Rather, control of pollution emissions will require a series of solutions tailored to the various classes of furnaces or boilers. Two

courses of action are available for development of the required control techniques: (1) improve current combustion equipment for short-term abatement, and (2) develop new burner systems for the future.

Domestic heaters are generally used in single-family homes and typically have an output of about 150,000 to 200,000 Btu/hr. These units are numerous and emit pollutants at ground levels in highly populated areas. However, the NO_x-concentration levels are lower than those of large boilers. The same is true of domestic incinerators. Control of nitrogen oxides and combustible particulates from these units will require a better understanding of the critical features of the burner and combustion chamber designs and the flame structure. Changes in design of nozzles, ignition units, air-introduction devices, pressure controllers, and fuel pumps offer ways of reducing emissions. Better control of heating cycles, improved combustor design, and fuel composition may also be important.

3. Industrial Furnaces

Large commercial heating units and industrial furnaces generally fall in the size range between domestic furnaces and utility boilers.[17,28] Methods of control developed for these two extremes will be generally applicable to industrial and commercial units. Flue-gas recirculation and "staged" combustion offer significant potential in such units.

Industrial furnaces in refineries, cement and lime kilns, glass manufacturing, and metallurgical operations represent a special class since their primary function is to provide heating at high temperatures. It is not generally possible to apply such methods as flue-gas recirculation and staged admission of air. Therefore, combustion-modification techniques using peak temperature reduction are not possible. NO_x control from these isolated single sources will require special consideration in keeping with the unique applications of the units.

In petroleum refineries or petro-chemical

processing, feed or process streams are heated in a controlled manner and they generally cannot be subjected to conditions that would result in thermal cracking or product degradation, as might occur on dilution or temperature reduction.

4. Incinerators

Refuse disposal by incineration results in NO_x emissions that may be significant locally.[29] For large units, emissions average about 25 ppm or approximately two to three pounds of NO_x per ton of refuse burned. It appears unlikely that reduction of NO_x emissions to lower levels can be achieved by process changes.

V

STACK-GAS CLEANING

The observations and conclusions of the Panel presented in this section are in general agreement with a recent study by ESSO Research and Engineering that included an assessment of existing and potential NO_x-control technology for stack gases.[17]

(a) If a flue-gas treatment process is required, aqueous scrubbing systems using aqueous alkaline solutions or concentrated sulfuric acid appear to offer potential for the control of both sulfur oxides and nitrogen oxides emissions.

(b) Selective catalytic reduction of NO_x with ammonia, hydrogen sulfide, hydrogen, or carbon monoxide is also a possibility.

(c) Silica gel, alumina, molecular sieves, chars, and ion-exchange resins all show some catalytic activity for oxidizing NO to NO_2, a step that is required in conjunction with any scrubber system to raise the NO_2/NO ratio to at least unity. However, the capacities are quite low at typical NO flue-gas concentrations.

(d) No flue-gas treatment process has so far been directly applied to NO_x-emission control in power plants.

(e) No catalyst has been found that is effective for a single low-investment NO-decomposition process, and the probability of discovering such a catalyst is small. In some reports of catalytic decomposition it appears that the NO_x was actually reacting with the "catalyst" or with a reducing agent rather than decomposing as such.

(f) Success in the removal of NO_x from combustion flue gases based on differences in physical characteristics such as molecular size, condensation temperature, or magnetic susceptibility appears to be highly remote.

Two systems that appear to offer the best possibility for removal of NO_x in the exit gases are magnesium oxide scrubbing and the Tyco modified lead-chamber process.[12,20,31] Catalyst systems being developed for automobile exhaust control may also be applicable in specific cases.

The low solubility of NO requires that NO_2 be added to the flue gas to form soluble N_2O_3 or that about half of the NO be oxidized to NO_2, in either magnesia scrubbing or the Tyco process. The use of two scrubbing systems to remove SO_x and NO_x in sequence is a major expense. However, the Tyco process has the potential for removing SO_x and NO_x simultaneously. Since NO_2 must be recycled to achieve the least equal parts of SO_2 and NO_2, the scrubber that removes NO_x must be highly efficient. For typical conditions (3,000 ppm SO_x) about 90-percent scrubber efficiency in NO_x removal is required just to keep the process going for SO_x removal even with no net NO_x removal. Ninety-nine percent efficiency is required to achieve a level of 50 ppm NO_x in the final stack gas, starting with an initial concentration of about 800 ppm. Estimates of the cost of the process are highly sensitive to the degree of removal of NO_x in the flue gas, assumed scrubber efficiencies, and the value of the sulfuric acid and nitric acid produced.

No proven process is available for substantial removal of NO_x from combustion stack gases. The Panel's definition of a proven process is one year of satisfactory operation on an industrial scale. Scrubber or adsorption systems proposed primarily for SO_x removal should also be evaluated for their potential in removing NO_x simultaneously.

Any wet scrubber system for NO_x removal will be expensive because:

(a) Most of the NO_x is in the form of NO, which is relatively unreactive and relatively insoluble. The maximum rate of absorption in an aqueous system occurs at a NO/NO_2 molar ratio of unity, which requires 1) recycle of NO_2 and a method of generating NO_2 from

the scrubbing system or 2) the oxidation of half of the NO to NO_2. The rate of oxidation of NO to NO_2 is slow and decreases with increasing temperature.

(b) Large vessels are required for scrubbing because of the large volume of gas that must be handled and the necessity for low-pressure drop.

Aqueous scrubbing systems, such as those using sulfuric acid, are in an early stage of development. It is necessary to generate NO_2 and recycle it to the scrubber in order to achieve practical rates of NO_x absorption, which in turn requires very high scrubbing efficiencies for substantial overall removal of NO_x.

Any new concepts showing potential for simultaneous removal of NO_x and SO_x should be encouraged, but their economic practicality should be carefully scrutinized.

It is deemed unlikely that a good absorbent can be found for removal of NO as such. However, any new ideas in this respect should be examined.

Catalytic reduction of NO_x to N_2 by a reducing agent such as ammonia as a process for treating stack gases from large utility boilers requires a sulfur-resistant catalyst if coal or oil is used as a fuel. Space velocity (i.e., catalyst activity) and catalyst life also limit this approach at present. Available information is insufficient to assess the potential of this method of control.

Decomposition of NO_x in the absence of a reducing agent requires such high temperatures, on even the best catalysts known, that it is impractical.

A substantial reduction in the amounts of NO_x released to the atmosphere (e.g., of the order of 50 to 80 percent) will come most economically from modifications of the combustion process rather than from scrubbing or adsorption systems to remove NO_x from stack gases.

VI

FORMATION AND CONTROL OF EMISSIONS FROM CHEMICAL OPERATIONS

Relative to emissions considered nationally, NO_x from chemical operations is quite small; but locally these emissions can be significant.[12,32,33] Essentially all these emissions are associated with the manufacture or use of nitric acid. About 75 percent of the nitric acid produced in the United States is consumed in ammonium nitrate production. The remainder is used in a variety of processes, with manufacture of adipic acid consuming 9 percent.

Because of the high ratio of NO_2 to NO in the stack gases from nitric acid plants, colored plumes are visible at relatively low NO_x levels, on the order of a few hundred ppm or much less, depending upon the stack diameter. The present method of control of emissions from nitric acid plants is primarily by catalytic reduction, using natural gas. It appears that, in much of the current practice, NO_2 is reduced only to NO. This is only decolorization, not emission control. Complete reduction to N_2 using methane requires complete burnout of the O_2 present, more consumption of natural gas, and closer control of the equipment. In addition, CO and hydrocarbon emissions increase with increasing NO reduction. Selective reduction of NO to N_2, using ammonia as a fuel, has been described, but there is insufficient information to determine whether this process is a practical alternative.

Scrubbing with caustic soda has long been practiced with NO_x emissions from nitration reactions, but it presents a disposal problem. Recent developments with molecular sieves[34] indicate that adsorption processes based on their use may be capable of reducing emissions to the 10 to 50 ppm level. In a nitric acid plant, the desorbed NO_2 can then be recycled to the absorption tower. *Evaluation of a molecular-sieve adsorption process on a large demonstration scale is timely.*

The quantities of NO_x emitted from nitric acid plants and chemical operations are but a small fraction of the total man-made emissions on a nation-wide basis; but they may comprise a significant local source of pollution. Technology for "decolorization" (conversion of NO_2 to NO) by catalytic reduction with natural gas is well established. Present methods of abatement (reduction to N_2) are available to reduce NO_x from typically 3,000 ppm to 100-500 ppm, but require careful control.[17] *Adsorption by molecular sieves or other adsorbents has been shown on a bench scale to result in even lower emission levels but no commercially proven process is yet available. Alkaline scrubbing is a proven process, but would involve liquid waste disposal problems.*

In some chemical processing with nitric acid, a substantial portion of the nitrogen oxides emitted may be in the form of N_2O. N_2O is believed to be innocuous and should be distinguished from NO and NO_2. N_2O is not included with NO_x-emission data.

VII

SAMPLING AND ANALYTICAL METHODS

Enforcing nitrogen oxide emission standards will require monitoring, as will enforcing particulate emission standards.[35] The circumstances are different from those associated with sulfur oxide emissions, in which fuel sulfur specification frequently has been satisfactory. The method recommended by EPA for 24-hour sampling of ambient NO_2 is the Jacobs-Hochheiser method.[3,4,5,6,7] Nitrogen dioxide is collected by bubbling air through a sodium hydroxide solution to form sodium nitrite. The nitrite ion is then detected colorimetrically by reacting the exposed reagent with phosphoric acid, sulfanilamide, and N-(1-Napththyl)-ethylenediamine dihydrochloride. Corrections must be made for SO_2 interference. Relative standard deviations are reported to be between 14 and 21 percent and no accuracy data are available. Alternate techniques such as the Saltzman method may differ by as much as a factor of 3. The Jacobs-Hochheiser method is for ambient-sample analysis and does not bear on the validity of source-sampling data.

Nondispersive infrared and electrochemical methods under development offer the potential of rapid analysis and improved accuracy. Photo-ionization or chemiluminescent procedures may also provide general-purpose portable detectors in the future.

Maintenance of emission and ambient air quality standards depends on accurate methods of sampling and analysis. Careful consideration must be given to the reliability of present methods of sampling and analysis for NO and NO_2, particularly in the presence of other pollutants. Sufficient attention should be paid to those problems to ensure that decisions are being made on the basis of well-established facts.

APPENDIX A

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